

## Chapter 22

# Oxidation of Organic Molecules with Molecular Oxygen Catalyzed by Heterometallic Complexes

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The reactions between  $[N(n\text{-Bu})_4][M(N)R_2Cl_2]$  (where  $M = \text{Ru, Os}$ ;  $R = \text{CH}_3, \text{CH}_2\text{SiMe}_3, \text{Ph}$ ) and chromate or other oxanions ( $\text{WO}_4^{2-}$ ,  $\text{ReO}_4^-$ ) produce stable but coordinately unsaturated heterometallic complexes. The Os-Cr and Ru-Cr heterobimetallic complexes  $[N(n\text{-Bu})_4][M(N)R_2(\mu\text{-O})_2\text{CrO}_2]$  are selective catalysts for the oxidation of alcohols with molecular oxygen. Heterotrimetallic complexes  $\{M(N)R_2\}_2(\mu_3\text{-S})_2M'(\text{dppe})$  (where  $M' = \text{Pt, Pd, Ni}$ ) result from the reactions between  $[N(n\text{-Bu})_4][\text{Ru(N)}R_2Cl_2]$  or  $[\text{Os(N)}R_2(\text{py})_2][\text{BF}_4]$  and  $M'(\text{SSiMe}_3)_2(\text{dppe})$ . The Ru-Pt complex  $\text{Pt}(\text{dppe})(\mu_3\text{-S})_2\{\text{Ru(N)Me}_2\}_2$  is a catalyst for the oxidation of alkenes and alcohols with  $\text{O}_2$ .

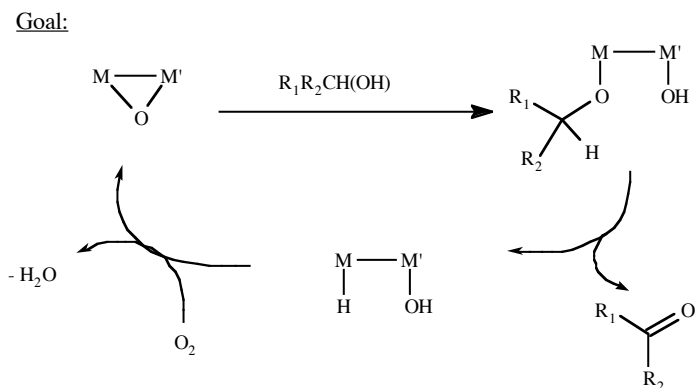
## Introduction

Oxidation reactions are important in the synthesis of organic compounds because these reactions create new functional groups or modify existing functional groups in a molecules. However, autooxidations and other reactions with radical intermediates frequently exhibit low chemo- and regioselectivity. Stoichiometric metal oxidants, such as  $\text{KMnO}_4$  or  $\text{K}_2\text{CrO}_4$ , and metal catalyzed reactions that use secondary oxidants, such as iodosylbenzene, amine-N-oxides, or hypochlorite salts, generate large quantities of waste. Recently, researchers have developed more environmentally friendly oxidation catalysts that use molecular oxygen.(i)

Heterometallic complexes are promising catalysts because the organic substrate and oxidizing agent could be activated by different metals within the same complex. Heterometallic catalysts may have advantages over monometallic catalysts if the metals act cooperatively in chemical transformations.(ii) Many heterometallic complexes have been prepared, including a few that show catalytic activity.(iii)

Our goal is to prepare heterometallic catalysts that will oxidize alcohols and other organic molecules in a selective manner using only molecular oxygen and releasing only water (*Scheme 1*). In the oxidation of alcohols for example, the alcohol O-H unit would add to a metal-oxygen bond. After  $\beta$ -hydride elimination, the oxidized product and water would be released and the metal complex reoxidized.

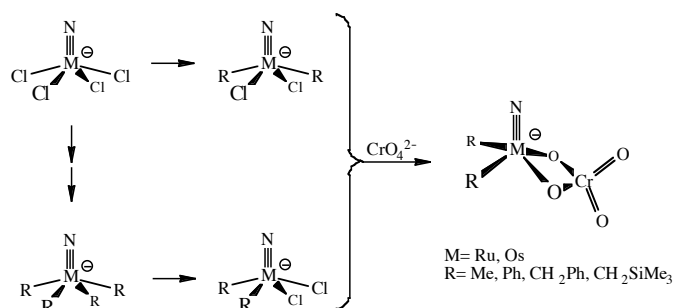
*Scheme 1*



## Results and Discussion

Anionic osmium(VI) and ruthenium(VI) complexes  $[\text{Os(N)(CH}_2\text{SiMe}_3)_2\text{Cl}_2]^-$ ,  $[\text{Os(N)Me}_2\text{Cl}_2]^-$ ,  $[\text{Os(N)Me(CH}_2\text{SiMe}_3)\text{Cl}_2]^-$ ,  $[\text{Ru(N)Me}_2\text{Cl}_2]^-$  or  $[\text{Os(N)Ph}_2\text{Cl}_2]^-$  react with aqueous potassium chromate or

Scheme 2



silver chromate to produce stable organometallic complexes containing a bidentate chromate group (Scheme 2).(iv) We have also prepared related oxanion complexes with  $\text{ReO}_4^-$ ,  $\text{WO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$  and tetrathiomallate complexes with  $\text{MoS}_4^{2-}$ ,  $\text{WS}_4^{2-}$ .(v)

The osmium-chromate complexes are stable in the presence of triphenylphosphine, cyclohexene, carbon monoxide, ethers, ferrocene, and dimethyl sulfide. This is surprising because chromium(VI) oxides are active oxidizing agents. They are capable of oxidizing triaryl- and trialkylphosphines, dialkyl sulfides, alcohols, aldehydes, alkenes, and even some activated hydrocarbons.(vi)

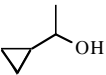

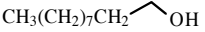
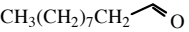
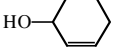
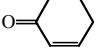
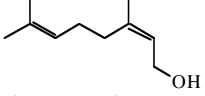
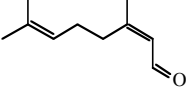
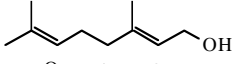
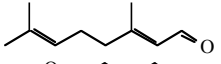
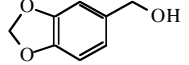
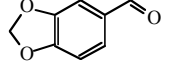
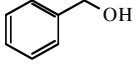
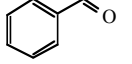
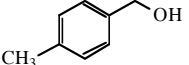
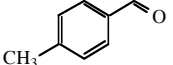
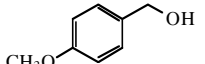
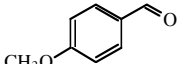
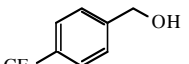
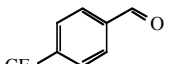
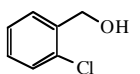
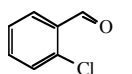
The complex  $[\text{N}(n\text{-Bu})_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\mu\text{-O})_2\text{CrO}_2]$  oxidizes benzylic, primary and secondary alcohols to the corresponding carbonyl compounds (Table 1).(vii) In air, these reactions are catalytic. Alcohol oxidation reactions are slow at room temperature and the rate of the reaction depends on the steric bulk of the alcohol. In competition experiments, primary alcohols are always oxidized faster than secondary alcohols. Oxidation of primary alcohols produces only aldehydes. There is no skeletal isomerization with the cyclopropyl-substituted alcohol. With unsaturated alcohols, there is no oxidation of the double bond and no isomerization.

To determine the mechanism of the reaction, we investigated reaction kinetics, characterized intermediate complexes, and examined the effects of isotopic substitution in the alcohol and molecular oxygen. The mechanism of alcohol oxidation with  $[\text{N}(n\text{-Bu})_4][\text{Os}(\text{N})(\text{CH}_2\text{SiMe}_3)_2(\mu\text{-O})_2\text{CrO}_2]$  proceeds through initial coordination of the alcohol at the osmium center, proton transfer,  $\beta$ -hydrogen elimination, and activation of molecular oxygen by the Os-Cr bond (Scheme 3). The rate of alcohol oxidation by all of the Os-Cr and Ru-Cr complexes was similar but did depend on both the metal, Os or Ru, and the ligands around that metal. Bulky alkyl groups on the osmium or ruthenium center reduced the rate of the alcohol oxidation reaction. Steric bulk at this metal would impede coordination of alcohol. For complexes with the same alkyl ligands, the Ru-Cr complexes are better catalysts than the Os-Cr analogs.

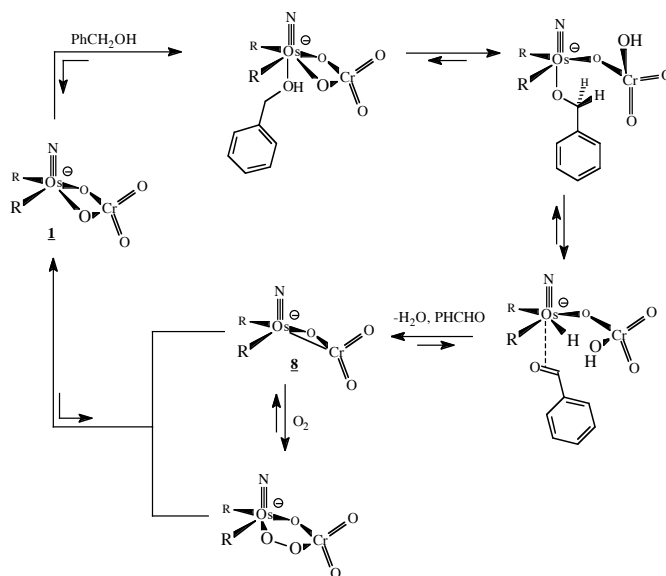
We have recently prepared chiral analogs of the Os-Cr alcohol oxidation catalyst and are exploring their activity in asymmetric oxidation reactions. We

are also examining oxidation reactions catalyzed by osmium and ruthenium complexes of perrhenate and tungstate oxyanions.

**Table 1. Catalytic Oxidation of Alcohols by  
[N(n-Bu)<sub>4</sub>][Os(N)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>(μ-O)<sub>2</sub>CrO<sub>2</sub>]**

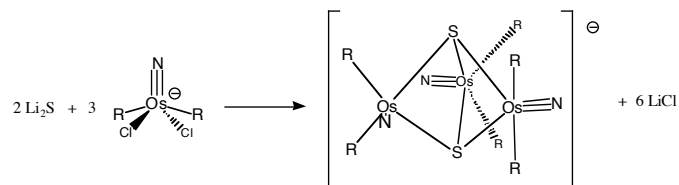
<i>Substrate</i>	<i>Product</i>
	
	
	
	
	
	
	
	
	
	
	

Scheme 3



In some instances, a trimetallic complex may be more effective than a bimetallic catalyst for the oxidation of organic molecules, provided that the metals are not coordinatively saturated. We prepared triosmium and triruthenium complexes in which the metals are in a high oxidation state (+6) and have a 16 electron count  $\{M(N)R_2\}_3(\mu_3-S)_2$  (Scheme 4).(viii) However, these homometallic complexes are catalytically inactive.

Scheme 4



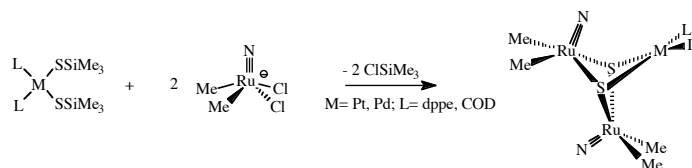
Studies of homogenous Ru-Pt heterometallic complexes in particular may improve our understanding of platinum-containing alloys in catalytic industrial processes and aid in the development of more efficient fuel cells.(ix) The addition of ruthenium to platinum catalysts greatly improves their activities for methanol oxidation and the activity is sensitive to structure.(x) Although a handful of Ru-Pt heterometallic complexes have been synthesized, only CpRu(PPh<sub>3</sub>)(μ-Cl)(μ-dppm)PtCl<sub>2</sub> is an electrocatalyst for methanol oxidation.(xi)

There are many strategies for synthesizing heterometallic complexes including bridge-assisted reactions. Sulfido ligands are common bridging groups in metal cluster complexes. Many of the rational syntheses of heteronuclear

compounds with bridging sulfido ligands involve displacing a ligand on a metal center with a terminal sulfido ligand on another metal.(xii)

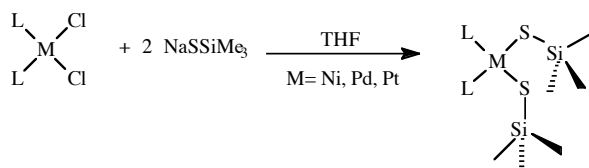
New, sulfido-bridged heterobimetallic complexes  $(dppe)Pt(\mu_3-S)_2\{Ru(N)Me_2\}_2$ ,  $(COD)Pt(\mu_3-S)_2\{Ru(N)Me_2\}_2$ , and  $(dppe)Pd(\mu_3-S)_2\{Ru(N)Me_2\}_2$  resulted from the reactions of  $(dppe)Pt(SSiMe_3)_2$ ,  $(COD)Pt(SSiMe_3)_2$ , or  $(dppe)Pd(SSiMe_3)_2$  with  $[PPh_4][Ru(N)Me_2Cl_2]$  (Scheme 5). The reaction between  $(dppe)Pt(SSiMe_3)_2$  and  $[Os(N)(CH_2SiMe_3)_2(NCMe)_2][BF_4]$  produced  $(dppe)Pt(\mu_3-S)_2\{Os(N)(CH_2SiMe_3)_2\}_2$ .(xiii) A similar reaction between  $(dppe)Ni(SSiMe_3)_2$  and  $[Ru(N)Me_2Cl_2]$  produced  $(dppe)Ni(\mu_3-S)_2\{Ru(N)Me_2\}_2$ .(xiv) Yields were moderate and ranged from 72 to 53% for the preparation of the trimetallic complexes. In all cases, the driving force for these reactions is the formation of a strong Si-Cl bond and elimination of trimethylsilylchloride. Due to the ease in which the Si-S bond can be cleaved by halides or oxygen nucleophiles, trialkyl- or trialkoxysilanethiolate complexes may be viewed as protected metal sulfides.

Scheme 5



The platinum, palladium, and nickel trimethylsilylsulfide complexes result from the reaction between  $NaSSiMe_3$  and the square planar dichloro complexes,  $(dppe)PtCl_2$ ,  $(COD)PtCl_2$ ,  $(dppe)PdCl_2$ , or  $(dppe)NiCl_2$  (Scheme 6). The  $dppe$  complexes form in high yield (83-87%) but the yield is lower (48%) for the more reactive cyclooctadiene complex.

Scheme 6



We determined the molecular structures of three of the heterotrimetallic complexes by X-ray crystallography. The structure of  $(dppe)Pt(\mu_3-S)_2\{Ru(N)Me_2\}_2$  is shown below. The platinum has a square planar coordination geometry and each ruthenium is in a square pyramidal coordination environment. The three metals and the two nitrido groups are in a plane with one sulfido ligand above and below this plane.

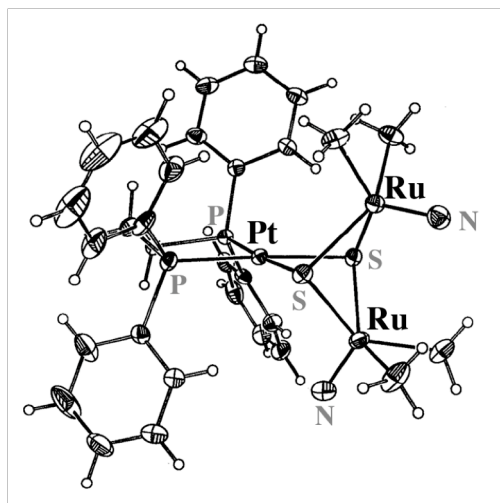
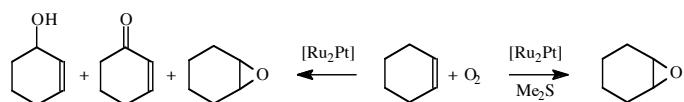


Figure 1. ORTEP Diagram of  $(dppe)Pt(\mu_3-S)_2\{Ru(N)Me_2\}_2$

The complexes  $(dppe)M(\mu_3-S)_2\{M'(N)R_2\}_2$  are catalysts for the oxidation of alcohols and alkenes with molecular oxygen. The rate of oxidation and the selectivity of the reactions depends on the nature of both M and M'. At 90 degrees, under an atmosphere of  $O_2$ , the osmium-containing complex  $(dppe)Pt(\mu_3-S)_2\{Os(N)(CH_2SiMe_3)_2\}_2$  is much slower in its oxidation of alcohols than is  $(dppe)Pt(\mu_3-S)_2\{Ru(N)Me_2\}_2$ . Oxidation of cyclohexene with  $(dppe)Pt(\mu_3-S)_2\{Ru(N)Me_2\}_2$  selectively produces cyclohexene oxide when the reaction is conducted in the presence of dimethyl sulfide and molecular oxygen but allylic oxidation products predominate when dimethyl sulfide is absent from the reaction mixture (*Scheme 7*).

Scheme 7



## Conclusion

We have prepared a series of sulfido-bridged trimetallic complexes of the form  $L_2M(\mu_3-S)_2\{M'(N)R_2\}_2$  where M is either platinum(II) or palladium(II) and M' is either ruthenium(VI) or osmium(VI). These complexes are soluble in a variety of organic solvents and stable to air and water. We are currently examining the oxidation of hydrocarbon and alcohol substrates with these complexes and molecular oxygen.

## Acknowledgements

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